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INT.CL. : C08B 37/08

TITLE : WATER-SOLUBLE CHITOSAN SALT AND PRODUCTION THEREOF

ABSTRACT : PURPOSE: To produce a water-soluble chitosan salt, having excellent stability for a long period due to water solubility within a neutral region and useful in the field of foods, cosmetics, paper, etc., by neutralizing an acidic aqueous solution of chitosan with a carbonate.

CONSTITUTION: An acidic aqueous solution of chitosan (e.g. aqueous solution prepared by adding and dissolving formic acid, acetic acid, hydrochloric acid, etc., in chitosan) is neutralized with a carbonate (e.g. ammonium carbonate or calcium carbonate) to afford the aimed water-soluble chitosan salt at pH 6–8. The above-mentioned chitosan salt is preferably freeze-dried into powder, which is then employed as an aqueous solution in use. For example, the chitosan salt can be used as a thickening agent or bacteriostatic agent by adding to a batter of fries in the field of food, further as a thickening agent or humectant in packs as cosmetic and as a brightener for paper surface and paper strength enhancer.

Documents
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Water soluble chitosan salt used for packing cosmetics, etc. - prepd. by neutralising acidic aq. soln. of chitosan with carbonate

Patent Number : JP01062302

International patents classification : C08B-037/08

• **Abstract :**
JP01062302 A Chitosan salt, which is water soluble at pH 6-8 is prepd. by neutralising an acidic aq. soln. of chitosan with carbonate.
Specifically, the acidic aq. soln. of chitosan is obtd. by adding organic salt (e.g. formic acid, acetic acid, lactic acid, sulphamic acid, etc., or inorganic acid hydrochloric acid, nitric acid, etc., to chitosan and dissolving the mixt. in water. The carbonate used is ammonium (bi)carbonate, Na (bi)carboante, K, (b)carbonate, Ca carbonate, etc. The neutralised aq. soln. is dried by freezing to form powder, which is dissolved in water before use.
USE/ADVANTAGE - The chitosan salt can be added as a thickener and bacteriastatic agent for the prepn. of a frying mixt., as a thickener and humidifier of packing agent in cosmetics and as a gloss agent and reinforcing agent for paper, because it does not coagulate protein. (0/0)

• **Publication data :**
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審査請求　未請求　発明の数 2　（全3頁）

⑤4発明の名称　水溶性キトサン塩およびその製造法

⑳特　願　昭62－218312
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明　細　書

1. 発明の名称

水溶性キトサン塩およびその製造法

2. 特許請求の範囲

1. キトサンの酸性水溶液を炭酸塩で中和して得られる、pH 6～8において水に可溶な水溶性キトサン塩。

2. キトサンの酸性水溶液を炭酸塩で中和することを特徴とするpH 6～8において水に可溶な水溶性キトサン塩の製造法。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は中性域において水溶性であるキトサン塩およびその製造法に関する。

〔従来の技術〕

キトサンは、甲殻類、昆虫、菌類等自然界に広く分布するキチンをアルカリ加水分解して得られる、D－グルコサミンがβ－1，4結合してなる塩基性多糖類である。そしてその特有の化学構造および性質から、凝集剤として余剰汚泥の脱水や水溶液の除濁などに広く使用され、さらに食品、化粧料、紙等の分野においても利用が期待されている。

ところで、キトサンは中性域では水不溶性であることから、これを水溶液とするには通常、ギ酸、酢酸、乳酸、スルファミン酸等の有機酸もしくは塩酸、硝酸等の無機酸の塩としたのち水に溶解させるか、またはこれらの酸の希薄水溶液に溶解させる方法がとられている。従つて、キトサンはpH 2～6の酸性水

溶液として種々の用途に用いられている。

〔発明が解決しようとする問題点〕

しかしながら、キトサンの水溶液が酸性であることは、多くの問題を生じ、キトサン自身の有用性が充分に発揮されず、自ずとその応用範囲は限定されていた。例えば食品、化粧料、紙等の分野においては、キトサンの水溶液が酸性であることから品質低下、製造技術上の問題が生じ使用が制限されていた。またキトサンの酸性水溶液は、長時間放置すると、徐々に加水分解をうけ、分子量の低下、粘度の低下が生じるという問題があつた。

従つて、キトサンの応用範囲を拡大し、安定性増大のために中性域において水溶性であるキトサン塩の開発が熱望されていた。

〔問題点を解決するための手段〕

斯かる実状に鑑み、本発明者は上記問題点を解決すべく種々検討したところ、キトサンの酸性水溶液に水酸化ナトリウム、水酸化アンモニウム等のアルカリを添加しても白濁もしくはゲル化を起こし中和することはできないが、炭酸塩を用いれば中和することが可能であり、キトサンの中性水溶液が得られることを見い出し、本発明を完成した。

すなわち、本発明はキトサンの酸性水溶液を炭酸塩で中和して得られる、pH 6～8において水に可溶な水溶性キトサン塩およびその製造法を提供するものである。

本発明の水溶性キトサン塩は、キトサンの酸性水溶液を炭酸塩で中和することにより製造される。

キトサンの酸性水溶液としては、例えばキトサンに蟻酸、酢酸、乳酸、スルファミン酸等の有機酸もしくは塩酸、硝酸等の無機酸を添加して溶解せしめた水溶液が使用される。

中和に用いる炭酸塩としては、例えば炭酸アンモニウム、炭酸水素アンモニウム；炭酸ナトリウム、炭酸水素ナトリウム、炭酸カリウム、炭酸水素カリウム等のアルカリ金属炭酸塩；炭酸カルシウム等のアルカリ土類金属炭酸塩等があげられる。これらの炭酸塩は単独で、もしくは二種以上を組み合せて用いることができる。

中和反応は、キトサンの酸性水溶液に炭酸塩の水溶液を徐々に添加すればよい。

炭酸塩水溶液添加終了時において、得られた本発明のキトサン塩の水溶液のpHは6～8である。

斯くして得られる本発明の水溶性キトサン塩は、上記の中性水溶液をそのまま食品、化粧料等の分野において利用してもよいが、水溶液を凍結乾燥して粉末とし、用時水溶液として使用するのが好ましい。

〔発明の効果〕

本発明のキトサン塩は、中性域において水溶性であるため、従来使用が制限されていた食品、化粧料、紙の分野においても何ら品質低下、製造技術上の問題点を生ずることなく利用できるものである。例えば食品の分野では、従来キトサンの酸性水溶液をフライ類の

パッターに添加することは、蛋白の凝固が起こることから不可能であつたが、本発明のキトサン塩はかかる問題がなく、増粘剤、静菌剤としてパッターに使用できる。また、化粧料の分野ではパック剤に増粘剤、保湿剤として使用できる。さらに紙の表面の光沢剤、紙力増強剤としても使用できる。

〔実施例〕

次に実施例を挙げて本発明を詳細に説明する。

実施例1

フローナックC（化粧品用キトサン，共和油脂工業製）6.0gを水300mlに分散させ、50%乳酸10.8gを添加して溶解させ、キトサン酸性水溶液（pH3.5）を得た。これに5%炭酸水素ナトリウム水溶液215mlを加え、pH7.0の白色コロイド状溶液を得た。

得られた白色コロイド状溶液を、凍結乾燥して白色粉末を得た。この粉末は0.5～4%濃度となるように水に溶かしたところ、透明な水溶液となつた。

実施例2

フローナックN（凝集剤用キトサン，共和油脂工業製）0.5gを水100mlに分散させ、これに90%酢酸0.33gを添加してキトサンの酸性水溶液（pH4.4）を得た。これに5%炭酸アンモニウム水溶液33gを滴下し、pH7.0の透明な溶液を得た。

濃度5000ppmの活性汚泥500mlに、この溶液5mlを添加した所、良好なフロックを生じ凝集剤として有効であつた。

実施例3

フローナックF（フイルム用キトサン，共和油脂工業製）6.0gを水300mlに分散させ、これに濃塩酸4.0gを添加してキトサンの酸性水溶液（pH2.0）を得た。これに炭酸カルシウム粉末3gを加え、更に2%水酸化アンモニウム水溶液30mlを加えてpH6.5の半透明溶液を得た。

得られた溶液を木材に塗布し、乾燥したところ、美麗な塗膜を形成した。

実施例4

フローナックN1.5gを水300mlに分散させ、これに90%乳酸1.3gを加えてキトサンの酸性水溶液を得た。これに5%$NaHCO_3$水溶液を加えてpH7.0の半透明のコロイド状溶液を得た。

比較例

フローナックC6.0gを水200mlに分散させ、50%乳酸10.8gを加えてキトサンの酸性水溶液を得た。これに5%$NaHCO_3$50mlを加えた後、更に2%NaOH47mlを加えてpH7.5にしたが白色の不溶沈殿が生じ、均一なコロイド溶液は得られなかつた。

以　上

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SPECIFICATION

1. Title of the Inv ntion

Water-soluble chitosan salt and a method for its production

2. Scope of the Patent Claim

1) A water-soluble chitosan salt which can be dissolved in water at pH from 6 to 8 which has been obtained by neutralising an acidic aqueous solution of chitosan with carbonate.

2) A method for the production of a water soluble chitosan salt which can be dissolved in water at pH from 6 to 8, characterized in that an acidic aqueous solution of chitosan is neutralised with carbonate.

3. Detailed Description of the Invention

Industrial Field of Application

The invention concerns a chitosan salt which is water soluble in the neutral region, and a method of its production.

Prior Art

Chitosan is obtained by subjecting chitin, which is widely distributed in the natural world in shells, insects and micro-organisms for example, to alkali hydrolysis. It is a basic polysaccharide in which D-Glucosamine is β-1,4 bonded. Thus, because of its unique chemical structure and properties, it is widely used as a coagulating agent for de-watering waste sludge and clearing aqueous solutions and, moreover, its use in the fields of foodstuffs, cosmetics and paper, for example, can also be anticipated.

However, chitosan is insoluble in water in the neutral range and so in general it is dissolved in water after forming a salt with an organic acid, such as formic acid, acetic acid, lactic acid or sulphamic acid for example, or with inorganic acid, such as hydrochloric acid or nitric acid for example, or it is dissolved in a dilute aqueous solution of such acids. Hence, chitosan is used in a variety of applications in the form of an acidic solution of pH from 2 to 5.

Problems to be Resolved by the Invention

However, the fact that the chitosan aqueous solution is acidic creates many problems, and the usefulness of chitosan itself cannot be realised satisfactorily and the range of applications for the material itself is limited. For example, in the fields of foodstuffs, cosmetics and paper the fact that the aqueous solution of chitosan is acidic lowers quality and give rise to problems with the manufacturing processes and

so its use is limited. Furthermore, an acidic aqueous solution of chitosan gradually undergoes hydrolysis on being left to stand for a long period of time, the molecular weight falls and there is a further problem in that the viscosity also falls.

Hence, the development of a chitosan salt which is water soluble in the neutral region is desirable for increasing the range of application of chitosan and also for increasing stability.

Problems to be Resolved by the Invention

The inventors have carried out various investigations on the basis of the situation outlined above with a view to resolving the abovementioned problems and it has been discovered that if an alkali such as sodium hydroxide or ammonium hydroxide, for example, is added to an acidic aqueous solution of chitosan then either a white turbidity is formed or gelling occurs and neutralisation in this way is impossible, but that neutralisation is possible if a carbonate is used, and the invention is based upon this discovery.

That is to say, the invention provides water-soluble chitosan which can be dissolved in water pH from 6 to 8, obtained by the neutralisation of an acidic aqueous solution of chitosan with carbonate, and a method its for the production.

A water-soluble chitosan salt of this invention is produced by neutralising an acidic aqueous solution of chitosan with carbonate.

An aqueous solution obtained by adding an organic acid, such as formic acid, acetic acid, lactic acid or sulphamic acid, or an inorganic acid, such as hydrochloric acid or nitric acid, to chitosan and achieving dissolution can be used as the acidic aqueous solution of chitosan.

Examples of the carbonate which is used for neutralisation include ammonium carbonate and ammonium bicarbonate; alkali metal carbonates such as sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate; and alkaline earth metal carbonates such as calcium carbonate. These carbonates can be used individually, or a combination of two or more types of carbonate can be used.

The neutralisation reaction should be carried out by slowly by adding an aqueous solution of the carbonate to an acidic aqueous solution of chitosan.

The pH of the aqueous solution of a chitosan salt of this invention obtained when the addition of the aqueous solution of carbonate had been completed is from 6 to 8.

With a water-soluble chitosan salt of this invention which has been obtained in this way, the abovementioned neutral aqueous solution may be used as it is in the fields of foodstuffs and cosmetics, for example, but the aqueous solution is preferably freeze dried to form a powder and made into an aqueous solution at the time of use.

Effect of the Invention

A chitosan salt of this invention is water soluble in the neutral region and so it can be used without giving rise to reduced quality or problems with the production process even in fields such as foodstuffs, cosmetics and paper where use has been limited in the past. For example, in the foodstuffs field the addition of the conventional acidic aqueous solution of chitosan to batter for frying purposes was impossible since it caused coagulation of the protein, but there is no such problem with a chitosan salt of this invention and it can be used in a batter as a thickening agent or as a [illegible] agent, for example. Furthermore, in the cosmetics field it can be used as a thickener or humectant in a pack agent. Moreover, it can also be used as paper surface glossing agent or as a paper reinforcing agent.

Illustrative Examples

The invention is described in more detail below by means of illustrative examples.

Example 1

Fronakku C (chitosan for cosmetic purposes, produced by Sanwa Oil and Fat Industries) (60 g) was dispersed in 900 ml of water, 10.8 g of 50% lactic acid were added and dissolution was achieved. A acidic aqueous chitosan solution (pH 3.5) was obtained. Then 215 ml of 5% sodium bicarbonate aqueous solution was added to the solution and a white colloidal solution of pH 7.0 was obtained.

The white colloidal solution so obtained was freeze-dried and a white powder was obtained. A clear aqueous solution was obtained when this powder was dissolved in water at a concentration of from 0.5 to 4%.

Exampl 2

Fronakku N (chitosan for coagulating agent purposes, produced by Sanwa Oil and Fat Industries) (0.5 g) was dispersed in 100 ml of water, 0.33 g of 90% acetic acid was added and an acidic aqueous solution of chitosan (pH 4.4) was obtained. Then 33 g of 5 % ammonium carbonate aqueous solution were added dropwise to the solution and a clear solution of pH 7.0 was obtained.

Good flocs were obtained when 5 ml of this solution were added to 500 ml of active sludge at a concentration of 5,000 ppm, and it was effective as a coagulating agent.

Example 3

Fronakku P (chitosan for film purposes, produced by Sanwa Oil and Fat Industries) (60 g) was dispersed in 900 ml of water, 40 g of concentrated hydrochloric acid were added and an acidic aqueous chitosan solution (pH 2.0) was obtained. Then 3 g of calcium carbonate powder were added to the solution and then 30 ml of 2% ammonium hydroxide were added and a semi-transparent solution of pH 6.5 was obtained.

The solution obtained was coated onto timber and dried and a beautiful coated film was formed.

Example 4

Fronakku N (1.5 g) was dispersed in 300 ml of water, 1.3 g of 90% lactic acid was added and an acidic aqueous solution of chitosan (pH 4.4) was obtained. Then 5% $NaHCO_3$ aqueous solution was added to the solution and a clear colloidal solution of pH 7.0 was obtained.

Comparative Example

Fronakku C (60 g) was dispersed in 200 ml of water, 10.8 g of 50% lactic acid were added and an acidic aqueous solution of chitosan (pH 4.4) was obtained. Then 50 ml of 5% $NaHCO_3$ aqueous solution were added to the solution, after which 47 ml of 2% NaOH were added and the pH was set to 7.5, but a white insoluble precipitate was produced and a uniform colloidal solution was not obtained.

The End

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Translator's Report/Comments

Your ref: 640204 (JP6462302) Your order of (date):

In translating the above text we have noted the following apparent errors/unclear passages which we have corrected or amended:

Page/para/line*	Comment
	The numerical values in the examples are poorly reproduced in the japanese text and should be read with this in mind.

* This identification refers to the source text. Please note that the first paragraph is taken to be, where rel vant, the nd portion of a paragraph starting on the preceding pag . Where the paragraph is stated, the line number relates to th particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.